Tracing Electronic Pathways in Molecules Using Inelastic Electron Tunneling Spectroscopy

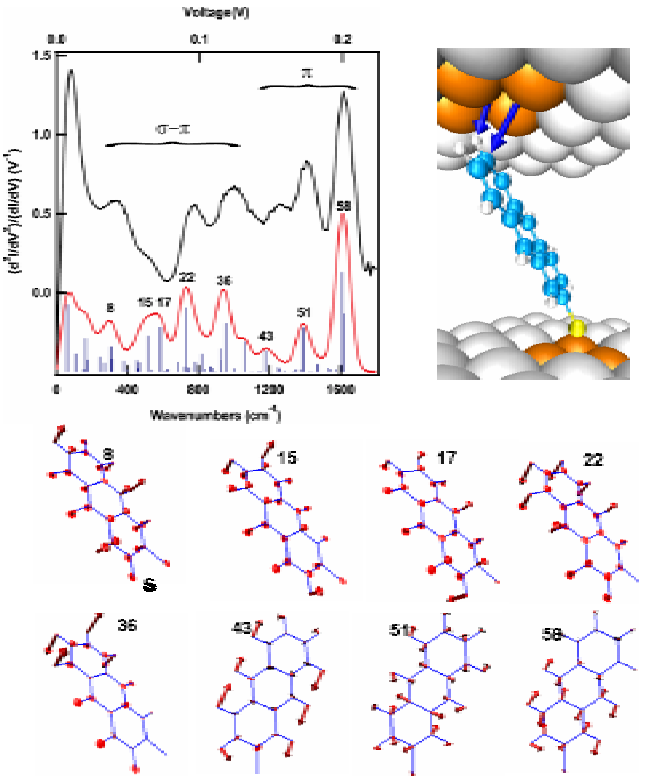
NIST researchers used inelastic electron tunneling spectroscopy (IETS) to measure the vibronic structure of non-equilibrium molecular transport, aided by a quantitative interpretation scheme based on non-equilibrium Greens function/density functional theory methods. Using this technique we are able to characterize the actual pathways that electrons traverse when moving through a molecule in a molecular transport junction.

J.G. Kushmerick, J.M. Beebe (Div. 837); R.D. van Zee (Div. 836); D.R. Stewart (Hewlett-Packard Laboratories); A. Troisi (University of Warwick); and M.A. Ratner (Northwestern University)

Molecular Electronics envisions that the nonlinear characteristics of individual or small ensembles of molecules will provide the active element in future electronic devices enabling some of the high-cost semiconductor fabrication processes to be replaced by low-cost chemical synthetic methods. A detailed understanding of charge transport across metal-molecule-metal junctions, the fundamental building block of a molecular electronic device, is paramount for molecular electronics to transition from a research endeavor into a viable technology. Our efforts have focused on the fundamental physical measurements which will provide the needed insight to enable the rational design of molecular electronic devices.

Using inelastic electron tunneling spectroscopy (IETS) to measure the vibronic structure of non-equilibrium molecular transport, aided by a quantitative interpretation scheme based on non-equilibrium Greens function/density functional theory methods, we are able to characterize the actual pathways that electrons traverse when moving through a molecule in a molecular transport junction. The pathways idea has been present in physical organic chemistry for years in connection with reaction mechanisms, and has been widely used in the interpretation of electron tunneling pathways in proteins, but no distinct observations have been made. We show that the IET spectra directly index electron tunneling pathways along the given normal coordinates of the molecule. One can then interpret the maxima in the IETS spectrum in terms of the specific paths that the electrons follow, as they traverse the molecular junction. IETS measurements therefore not only prove (by the appearance of molecular vibrational frequencies in the spectrum) that the tunneling charges in fact pass through the molecule, but also can be used to determine just what the transport pathways are, and how they change with the geometry and placement of molecules in junctions.

Future Plans: We plan to use this strong coupling of inelastic electron tunneling spectroscopy and quantitative interpretation scheme to determine the pathways for charge transport in molecules with more complex chemical and electronic structures. The over riding goal is that through detailed understanding of the fundamental processes in charge transport across molecular junctions rational design of molecular devices will become a reality.



Experimental (black) and computed spectra (red) of an anthracene thiol junction. The observed normal modes belong to two groups: out of plane modes that favor the intercommunication between the σ and π tunneling channels and in plane C-C stretches that modulate the main π-type tunneling channel. The molecules couple to the electrode via the s orbital of the hydrogen and the p_z orbital of the carbon.

Publication in Preparation: A manuscript describing these findings has been completed and will submitted for publication. These results have also been disseminated to the Defense Advanced Research Projects Agency, which provided partial funding for this research.